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ON THE POSSIBLE ROLE OF SMALL POLARONS IN THE CHARGE AND ENERGY TRANSPORT IN THE α-HELIX PROTEINS

D. Čevizović, S. Zeković, Z. Ivić

Institute for Nuclear Science «Vinča», Belgrade, Serbia

We study the possibility of the small-polaron creation in α-helix proteins, accounting for the self-trapping of the intramolecular vibration energy quanta. The small-polaron concept of energy transfer in polypeptides has been revisited on the basis of these results. It was found that traditional small-polaron theories cannot be directly applied to the vibrational quanta transfer in these substances. In particular, true eigenstates of the system should correspond to a partial dressed polarons rather than to the fully dressed small-polaron states.

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INTRODUCTION

The mechanism of long range intramolecular vibrational energy transfer in biological macromolecules, like DNA and α-helix, has been an attractive area of investigation over the last 30 years. But, in spite of the all efforts, this problem remains unresolved!

Attractive explanation on the microscopic level has been proposed in mid seventies by Davydov and coworkers [1]. The essence of that theory is the assumption that energy released in the hydrolisis of ATP can be captured by the protein molecules and then transported along the polypeptide chain in a soliton form which arises due to the self-trapping (ST) of the amide-I (or C=O stretching) quanta. However, due to the lack of direct experimental evidence of soliton existence in these substances, Davydov's idea for a long time has been considered just as an interesting theoretical concept.

Situation changed at the begining of eighties when G. Gareri and A. Scott suggested [2] that appearance of the so-called unconventional amide-I band, observed in a previous year experiment by Careri in crystaline acetanilide (ACN) [3], may be explained in terms of Davydov's soliton theory (DST). Their ideas have encouraged restored interest in DST [1, 4–7]. However, the original Davydov's concept should be substantially modified since the values of basic energy parameters in these substances fall into nonadiabatic weak coupling regime [5]. For these reasons an alternative interpretation of Careri's experiments in terms of small-polaron (SP) theories has been proposed [4]. Since then, ST in biological systems has been investigated within the SP models of Holstein and Lang–Firsov (LF) transformation. However, their concept relies upon the assumption of fully dressed excitations which is not justified in realistic substances due to weakness of vibron–phonon interaction. Therefore, although correct in principle, this alternative approach should be modified since partially dressed SP states rather than fully dressed ones should be the true eigenstates of the system. In this paper we offer an improved treatment of the ST in biological substances. It is based upon the modified Lang–Firsov (MLF) transformation and Bogoliubov theorem [8–10]. Optimization procedure was carried out in the region of parameter space which corresponds to the values of system parameters usually employed in the theoretical examination of energy transfer in polypeptides [4, 11, 12]. Conditions for the small-polaron formation are formulated in terms of the values of the temperature and basic energy parameters of system.

THEORETICAL ANALYSIS

The theoretical framework of our analysis is 1D Holstein's Hamiltonian

$$H = \Delta \sum_n A_n^\dagger A_n - J \sum_{n,\delta=\pm 1} A_n^\dagger A_{n+\delta} + \sum_q \hbar\omega_q B_q^\dagger B_q + \\ + \frac{1}{N} \sum_{q,n} F_q \, \mathrm{e}^{iqnR_0} A_n^\dagger A_n (B_q + B_{-q}^\dagger), \quad (1)$$

where Δ is vibron excitation energy, $A_n^\dagger (A_n)$ describes presence (absence) of the vibron quanta on nth lattice site, $B_q^\dagger (B_q)$ creates (annihilates) phonon quanta, J denotes intersite transfer integral, ω_q is phonon frequency, and R_0 is lattice constant. $F_q = F_{-q}^*$ denotes vibron-phonon coupling parameter, and in the case when vibrons interact with optic phonons it has the form $F_q = \chi\sqrt{\hbar/2M\omega_q}$. Phonon dispersion law for optic phonons has the form $\omega_q = \omega_0\sqrt{1 + \Omega \cos qR_0}$, where $\Omega = \omega_1^2/\omega_0^2$.

The character of these states (if any arise!) is determined by mutual relationships between values of the basic energy parameters of the system: characteristic phonon energy, $\hbar\omega_0$, quasiparticle energy bandwidth $2J$, and SP binding energy $E_b = \dfrac{1}{N} \sum_q \dfrac{|F_q|^2}{\hbar\omega_q}$. In particular, just two parameters characterize the ST in these media. They are adiabatic parameter $B = 2J/\hbar\omega_0$ and coupling constant $S = E_b/\hbar\omega_0$.

In nonadiabatic lines, adiabatic parameter is small ($B \ll 1$). This condition is satisfied in crystals with narrow energy band or in the case of small value of intersite transfer integral. In that case quasiparticle and lattice deformation form new entity: we have dressed quasiparticle, with new effective mass, and with reduced energy band. In this case lattice distortion is concentrated around a small number of lattice sites (nonadiabatic SP). Theoretical description of those systems is based on the methods that employ unitary transformation (most frequently Lang–Firsov (LF) transformation).

System parameters that characterize α-helix proteins suggest that vibron ST would result in the creation of the weakly dressed nonadiabatic SP (in ACN, in the case of C=O stretch mode that interact with optic phonons, system parameters have the following values [4, 11, 12]: $B = 0.16$ and $S = 0.1$, while in α-helix these parameters have the following values: $B = 0.3$ and $S = 0.04$). Consequently α-helix proteins may be successfully described by means of the MLF theory, based upon apliance of unitary transformation operator $U = \exp\left\{-\frac{1}{\sqrt{N}}\sum_{q,n} f_q\,\mathrm{e}^{-iqnR_0}A_n^\dagger A_n(B_{-q} - B_q^\dagger)\right\}$, where f_q is variational parameter whose magnitude defines the degree of dressing and the character of ST states. In the wave number representation transformed Hamiltonian has the form $\tilde{H} = U^\dagger H U = \sum_k E_{SP}(k)a_k^\dagger a_k + \sum_q \hbar\omega_q b_q^\dagger b_q + \tilde{H}_{\mathrm{int}}$ where a_k is Fourier transform of $a_n = U^\dagger A_n U$ which describes new quasiparticles (polarons), $b_q = U^\dagger B_q U$ describes new phonons in the chain with shifted equilibrium position of the molecular group, $E_{\mathrm{SP}}(k) = \Delta - \mathcal{E}(T) - 2J\,\mathrm{e}^{-S(T)}\cos(kR_0)$ is SP band energy, $\mathcal{E}(T) = \frac{1}{N}\sum_q \left\{\left(f_q + f_{-q}^*\right)F_q - \hbar\omega_q\left|f_q\right|^2\right\}$ is temperature-dependent SP energy shift, $S(T) = \frac{1}{N}\sum_q \left|f_q\right|^2(2\bar{n}_q + 1)(1 - \cos(qR_0))$ is quasiparticle band narrowing factor, and $\bar{n}_q = \left(\mathrm{e}^{\hbar\omega_{\mathrm{q}}/\mathrm{k_B T}-} - 1\right)^{-1}$.

The temperature-dependent screening factor $Z = \mathrm{e}^{-\mathrm{S(T)}}$ measures the coherence of transfer of the vibrational energy of the intramolecular mode from site to site, and it is proportional to inversion value of polaron effective mass.

Optimal forms of variational parameters are determined in accordance with the Bogoliubov theorem by means of the minimization of the model free energy of the system. Thus we have

$$f_q = \frac{F_q^*}{\hbar\omega_q + 2J\,\mathrm{e}^{-S(T)}(2\bar{n}_q + 1)(1 - \cos(qR_0))}. \tag{2}$$

Obtained results for variational parameters are very similar with parameters that appear in standard LF approach: $f_q^{\mathrm{LF}} = F_q^*/\hbar\omega_q$. Comparing f_q and f_q^{LF}, one can see that, actually, LF approach is equivalent with MLF approach in the limit

$S(T) \to \infty$. This is the case of heavy dressed quasiparticles. Introducing (2) into relations for $S(T)$ and $\mathcal{E}(T)$ we obtain:

$$S(\tau) = S\sqrt{1-\Omega^2} I_S(\tau), \quad \mathcal{E}(\tau) = \hbar\omega_0\sqrt{1-\Omega^2}\left(2I_1(\tau) - I_2(\tau)\right), \tag{3}$$

where $\tau = k_B T/\hbar\omega_0$ is normalized temperature, and integrals that appear in above relations have following form: $I_S(\tau) = \dfrac{1}{\pi}\displaystyle\int_0^\pi \dfrac{(1-\cos x)\,\mathrm{cth}\left(\dfrac{\sqrt{1+\Omega\cos x}}{2\tau}\right)}{\sqrt{1+\Omega\cos x}\,\{\Sigma(\tau,x)\}^2}dx$, $I_1(\tau) = \dfrac{1}{\pi}\displaystyle\int_0^\pi \dfrac{dx}{\sqrt{1+\Omega\cos x}\,\{\Sigma(\tau,x)\}}$, $I_2(\tau) = \dfrac{1}{\pi}\displaystyle\int_0^\pi \dfrac{dx}{\{\Sigma(\tau,x)\}^2}$, and $\Sigma(\tau,x) = \sqrt{1+\Omega\cos x} + B\,\mathrm{e}^{-S(\tau)}(1-\cos x)\,\mathrm{cth}\left(\dfrac{1}{2\tau}\sqrt{1+\Omega\cos x}\right)$.

At this stage, it is necessary to compare SP energy obtained by LF method and MLF method

$$\frac{E_{\rm gs}^{\rm LF}}{\hbar\omega_0} = -S - B\,\mathrm{e}^{-S}, \quad \frac{E_{\rm gs}^{\rm MLF}}{\hbar\omega_0} = -\mathcal{E}(T=0) - B\,\mathrm{e}^{-S(T=0)}. \tag{4}$$

In such a way we obtain a boundary in (S, B) plane which separates those values of system parameters corresponding to fully and partially dressed SP states. Latter one corresponds to all points lying above this line. In Fig. 1. we have visualized the afore-mentioned boundary line in (S, B) plane. Obviously, vibron ST for ACN and α-helix results in creation of partially dressed SP states.

Let us now focus on SP effective mass as a function in dependence of temperature and system parameter values which characterizes all SP properties. For that purpose we analyze the SP screening parameter versus S, B, and temperature. It is graphically presented on Fig. 2. Each curve on Fig. 2 *a* corresponds to one

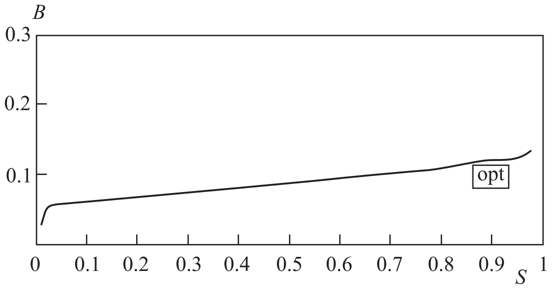

Fig. 1. Fully dressed versus partial dressed states boundary in system parameter space

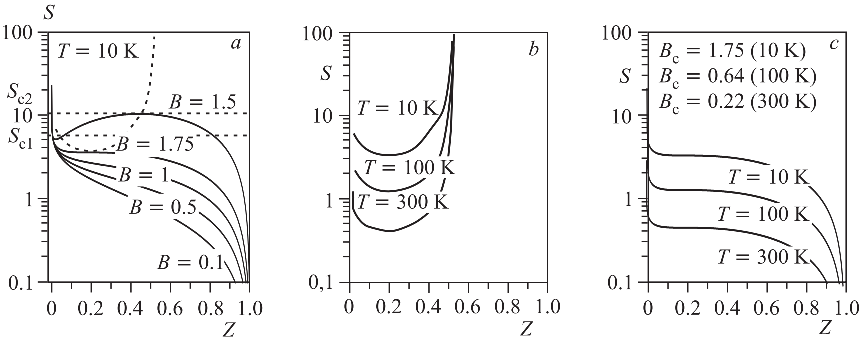

Fig. 2. *a*) The set of adiabatic curves for $T = 10$ K are presented by full lines. Dashed line corresponds to stability curve. *b*) The set of three stability curves, for different system temperatures. *c*) The set of three critical adiabatic curves

value of adiabatic parameter. Dashed line corresponds to stability curve – that curve is the locus of the points where the first derivative of $S(Z)$ vanishes. It also corresponds to the set of points where the second derivative of E_{gs} vanishes. All the points lying below stability line define a stable SP states, while those lying above that define the unstable states. SP screening factor Z is one-valued function of S for small values of B. However, for all $B > B_C$, there are three values of Z for given S. This physically means that for $B < B_C$, there occurs the continual transition of partially dressed polaron band states towards ST (immobile) SP of infinite mass as S increases. For each adiabatic curve defined by means of $B > B_C$, there exists a metastable region corresponding to the coexistence of free (partially dressed) and localized SP states with an abrupt transition between them. This region is bounded by two critical coupling constants S_{C1} and S_{C2}. This abrupt change is more expressed in the highly adiabatic region where a slightly dressed, practically free band state transits into a ST state. With temperature increase critical value of adiabatic parameter decreases.

CONCLUSIONS

Based on the results presented, we made the revision of SP concept of energy transfer in polypeptides. We found that traditional SP theories cannot be directly applied to the vibrational quanta transfer in these substances. Our analysis shows that the existing vibron transfer theories should be modified in accordance with partial dressing strategy, because vibron self-trapping would result in formation of partialy dressed polarons, rather than to the fully dressed SP states.

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